Hydrogen production over molybdenum loaded mesoporous carbon catalysts in microwave heated reactor system

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ABSTRACT

Ammonia decomposition reaction to produce COx free hydrogen over molybdenum incorporated mesoporous carbon based catalysts was studied in a microwave heated reactor system. Mesoporous carbon is acting as the catalyst support as well as the microwave receptor in the reaction medium. While the highest conversion value was 49% in conventionally heated reaction system at 600 °C, total conversion value was achieved over the same catalyst at 400 °C in microwave heated system with a GHSV of 36,000 ml/hg$_{cat}$. Transfer of microwave energy directly to the active particles, volumetric heating and hot spot formation are the main reasons of this great enhancement. While molybdenum nitride was observed under conventional heating, molybdenum carbide was formed in case of microwave application which could be another improving effect on catalytic activity of molybdenum incorporated mesoporous catalysts.

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1. Introduction

Various studies on the production of COx free hydrogen from ammonia have been carried out by different research groups using the reactor systems equipped with the conventional heating systems, since COx components that have been produced during the synthesis of hydrogen from either steam reforming or other routes that are mainly based on hydrocarbons, cause a decrease in fuel cell performance, i.e. poisoning effect [1–3]. As it is known, ammonia is commonly used in industrial process such as in the production of fertilizers, urea etc. [4]. During these processes, excessive amount of ammonia is being emitted to the atmosphere or discharged with wastewater effluent streams. Therefore, removal and recovery of ammonia is an important issue to prevent water and environmental pollution [5,6]. Nowadays, conversion of ammonia to hydrogen via decomposition reaction has been also considered as an alternative route to the conventional treatments to decrease the concentration of ammonia in wastewater [5,4].

Microwave energy (having a frequency value of 2.45 GHz) has been used as an alternative heating method to enhance the heterogeneous chemical reactions. Heat is generated by direct conversion of electromagnetic energy where it is needed in microwave sys-

tems, unlike conventional heating methods, which are based on heat transfer from the source mainly by means of conduction and convection modes [7–10]. Studies on the microwave focused reaction systems showed that higher yields, improved selectivities, lower coke formation and higher stability due to the selective, volumetric and non-contact heating properties of microwave heating systems [7,8,11–14]. Since the particle is directly heated, less time is required to reach the desired temperature and control of heating would be much easier in the reaction medium [15]. In the literature there is a variety of chemical reactions that have been tested in microwave heating system, such as decomposition [7], pyrolysis [16] and dry reforming of methane [17], biodiesel production from soybean oil [18], autothermal reforming of methanol [19], steam reforming of ethanol [14] and methanol [20], water gas shift reaction [21], pyrolysis of coal [22] and so on. As seen in this summary, eventhough different studies were reported for hydrogen production from hydrocarbons, an application of microwave reactors for the ammonia decomposition reaction was limited in the literature. In our previous study, which was the pioneer work of the microwave reactor application to ammonia decomposition reaction to produce COx free hydrogen, iron based mesoporous catalysts were tested in microwave focused reaction system and complete conversion of ammonia was achieved at 450 °C over the catalyst having 7.7 wt% Fe with a GHSV of 36,000 ml/hg$_{cat}$. On the contrary, when the conventionally heated reactor was used complete conversion of ammonia was achieved at 600 °C [23]. It is

known that, in microwave heated system, a dielectric material should be present either as a catalyst itself or as a microwave receptor to absorb microwave energy beside the selected catalyst [11]. Carbonaceous materials are known as being strong absorbers of microwave and they could convert microwave energy to thermal energy resulting in an increase in temperature [17,9,22]. For this reason, in our studies carbonaceous material, namely mesoporous carbon, has been selected in the preparation of the catalysts.

In ammonia decomposition reaction, different transition metals, such as Fe [24–27], Ni [28], Co [29–31], and nobel metals, such as Ru [32–34], were used and Ru incorporated catalysts were found to be the most active ones [1,2,32]. Transition metal nitrides and carbides are being considered as interstitial compounds and their catalytic characteristics have similarities with Group VIII noble metals which were firstly described in the pioneering work of Levy and Boudart [35]. Besides this property, their lower cost makes them potential catalysts for different reactions such as isomerization, hydrogenation, ammonia synthesis [35–38]. In addition to the different researches related to the application of molybdenum carbide in the hydrogen production from hydrocarbons with high efficiency, which was reviewed recently by Ma et al. [39]; a few studies on the bulk or MCM-41, CNT or Al_2O_3 supported molybdenum nitride and carbide compounds with or without promoter have been found in the literature for the conventional heated ammonia decomposition reaction [40–45]. In these studies, generally, a reaction temperature of 600 °C or higher was required to obtain ammonia conversion values over than 70% when ammonia was feed to the reaction system with a GSHV of 36,000 h^{-1} or much lower values. Eventhough these studies indicate that molybdenum based catalysts are highly promising for COx free hydrogen production; to the best of our knowledge, the application of alternating heating system such as microwave radiation to the ammonia decomposition reaction over molybdenum nitride or carbide catalysts, has not been recognized.

Therefore, in the present study, hydrogen production from ammonia was investigated in a focused microwave heated system over the molybdenum loaded mesoporous carbon catalysts and the results were compared with the corresponding results obtained in a conventionally heated tubular reactor. Result of this study would be important to get an idea of the application of microwave heating system to ammonia decomposition reaction over catalysts prepared by using different transition metal catalysts.

2. Experimental

In the synthesis of catalysts, impregnation procedure was followed. As a support material, mesoporous carbon (99.95% purity, Sigma Aldrich) was selected due to its microwave receptor ability in converting electromagnetic energy into heat and 0.5 g of it was dissolved in ethanol solution (vol 20%) to mix with molybdenum salt solution, which was prepared by using Ammonium Molybdate ($H_{24}Mo_7N_6O_{24}$, Sigma Aldrich). The final synthesis solution was stirred at 60 °C at a rate of 280 rpm for 3 h, then, it was dried at 80 °C in a conventionally heated oven for 10 h. The solid products were treated at 700 °C for 5 h under the flow of nitrogen (60 ml/min). The synthesized samples were called as Mo@MC(X), where X referred to % ratio (in wt) of Mo to the total amount of solid (Mo and mesoporous carbon) used in the preparation of synthesis solution and it was changed in the range of 5–15. Before the reaction studies, samples were reduced under the flow of pure hydrogen at 600 °C for 2 h.

Synthesized catalysts were characterized by applying different techniques. The exact metal content of the synthesized catalysts was determined by Inductively Coupled Plasma (ICP) analyses which were carried out using Perkin Elmer DRC II model ICP-OES

equipment. Nitrogen adsorption-desorption analyses were performed at 77 K, using the Quantachrome Autosorb-6B instrument. Before each analysis, samples were degassed at 200 °C for 3 h. The surface area values of the catalysts were calculated using the Brunauer, Emmett and Teller (BET) method and pore size distributions were calculated by applying the BJH method to the desorption isotherm. In order to determine crystal structure of the synthesized catalyst, powder X-Ray diffraction (XRD) analyses were performed by a BRUKER-AXS D8 ADVANCE A 25 diffractometer with a CuKα radiation source. The instrument was operated at 40 kV voltages and 40 mA current and the diffractograms were recorded in the range 5–90° with steps of 0.02°. Average crystallite sizes were calculated by Scherrer formula, $D = (K^*\lambda)/(\beta^*\cos\theta)$, where K = 0.89, λ = 0.154056 nm, β was the full width at half maximum of diffraction peaks and θ was the Bragg angle. Joint Committee of Diffraction Data (JCPDS) and International Centre for Diffraction Data (ICDD) database were used in the evaluation of the diffractograms. The texture of the synthesized catalysts was determined by JEOL JEM 2100F High Resolution Transmission Electron Microscope (HRTEM) with a maximum acceleration voltage of 200 kV. Samples were dispersed in ethanol and one drop of this suspension was deposited on a grid covered by C-film to carry out analysis.

Reaction studies were carried out using Microwave system (SAIREM Co.) with a maximum working power of 2 KW and a frequency of 2.45 GHz. The detail of microwave reactor system is presented in Fig. 1. A fixed bed quartz tubular reactor having an inner diameter of 13 mm was used, remembering that quartz reactors were transparent to microwaves [14]. In each experiment, 0.1 g of reduced catalyst was placed in the middle of the quartz tubular reactor and microwave power was directly focused to this catalytic bed portion. By changing the power source, the reaction temperature was adjusted to the desired value. Infrared pyrometer (Raytek M13) was used in temperature measurement and it was placed at a location looking directly to the catalyst bed. The microwave forward (FP) and reflected power (RP) profiles, recorded during the reaction period with the corresponding observed temperature is presented Fig. 2. which is common for all the synthesized catalysts. In a very short time interval, in seconds, temperature was increased to the desired value by fine adjustment of the microwave power and kept stable throughout the reaction study. Generator power was set to 80 W in all experiments in order to change temperature from 250 °C to higher values, but, amount of power absorbed by the catalysts, which was calculated by the difference between FP and RP values, was lower than this value and the rest of microwave was absorbed by the cooling water. It was about 10 W or less power, which is not provided exactly due to the precision of instrument is 0.01 W or higher, sufficient for heating the synthesized catalysts up to 500 °C. After this point, it was observed that absorbed amount power by the catalysts was increased to about 10–50 W changing with the catalysts prepared at different Mo loading. In order to ensure safe working environment, a MW leakage detector (SAIREM Company) was used through out the reactions.

Molybdenum incorporated mesoporous carbon catalysts were also tested in conventionally heated system in order to make a comparison between two heating systems. In this case, quartz reactor, having 0.1 g of fresh reduced catalyst in its middle portion, was placed in temperature controlled electrically heated tubular furnace (Protherm).

High purity gaseous ammonia (99.95%) was fed to the reactor at a flow rate of 60 ml/min (GHSV of NH_3: 36,000 ml/g_{cat}h) in both of the systems. Analysis of unconverted ammonia and the products, namely hydrogen and nitrogen, were carried out by using an online Gas Chromatograph (SRI), equipped with Thermal Conductivity Detector (TCD) operated at 180 °C. Argon was selected as the carrier gas for gas chromatograph and it was sent at 17 psi. Porapak Q packed column in 1.5 m length was used and it was kept at 30 °C.
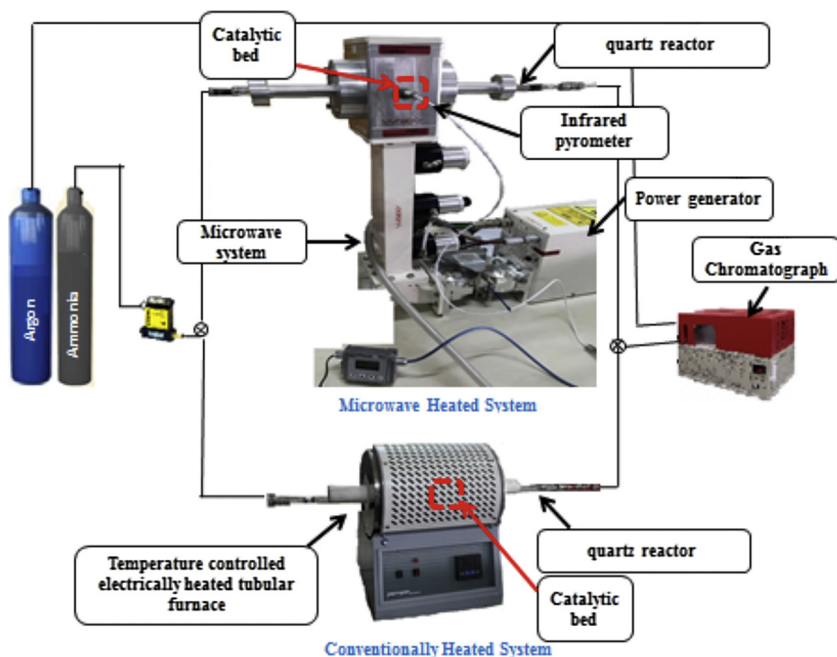
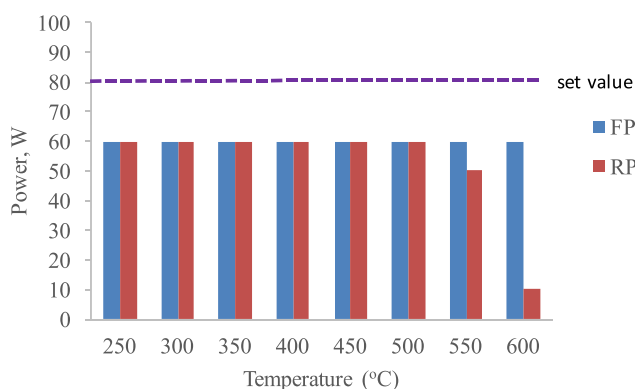**Fig. 1.** Schematic representation of experimental setup.

Fig. 2. Microwave power profiles, set value, forward power (FP), reflected power (RP) recorded during the reaction.
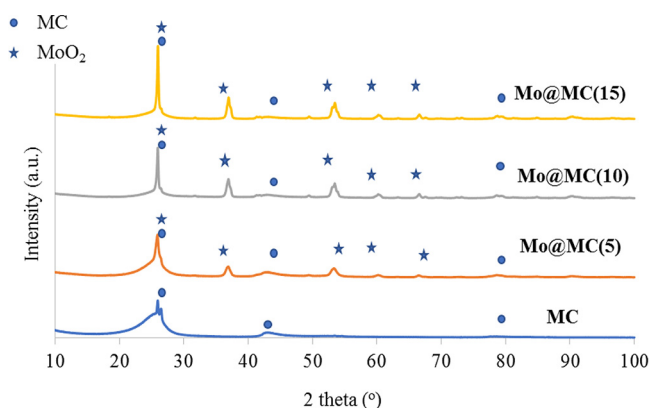

Fig. 3. XRD results of molybdenum incorporated mesoporous carbon catalysts at different metal loadings in their calcined form.

Conversion of ammonia to hydrogen (X) was evaluated basing on the data taken form the effluent stream provided by gas chromatograph and calculated using equation (Eq. (1)) with the contribution of nitrogen mass balance (Eq. (2)). In these expressions F_{NH3} and F_{N2} referred to unconverted amount of ammonia and produced amount of nitrogen, respectively, these were the data provided by the Gas Chromatograph. Total amount of ammonia before the reaction, F_{NH3}^0, was calculated from nitrogen mass balance. After reaching steady state at the desired temperature value, at least four successive measurements were carried out, each one took 15 min, and conversion profiles were built using average of them. Conversion values evaluated in these repeated runs were all within ±5% error limits.

$$X = \frac{F_{NH3}^0 - F_{NH3}}{F_{NH3}^0} \times 100 \tag{1}$$

$$F_{NH3}^0 = F_{NH3} + 2F_{N2} \tag{2}$$

3. Results and discussion

3.1. Catalyst characterization results

X-ray diffraction patterns of the molybdenum incorporated mesoporous silicate catalysts in their calcined form, as well as, that of pure mesoporous carbon (MC) are presented in Fig. 3. High intensity peak observed at 2θ values of 25.90° with the lower intensity ones at 2θ value of 43.09° and 78.03° in the diffraction lines of the synthesized catalysts were belonging to pure mesoporous carbon, according to JCPDS card 00-041-1487. Indeed, it is known that graphite like structures play an important role in the evaluation of the dielectric properties of mesoporous carbon. Electrons in graphite's layer structure are able to move freely and generate an inductive current in the electromagnetic field causing a loss current and energy dissipation [46]. So, the degree of graphitization is one of the factors that affect the microwave absorbing properties of carbon materials and as indicated by Du et al. [47] mesoporous carbon having suitable degree of graphitization and uniform pore structure could be used as an excellent microwave absorber. In the present study, the dielectric loss tangent, which is defined as
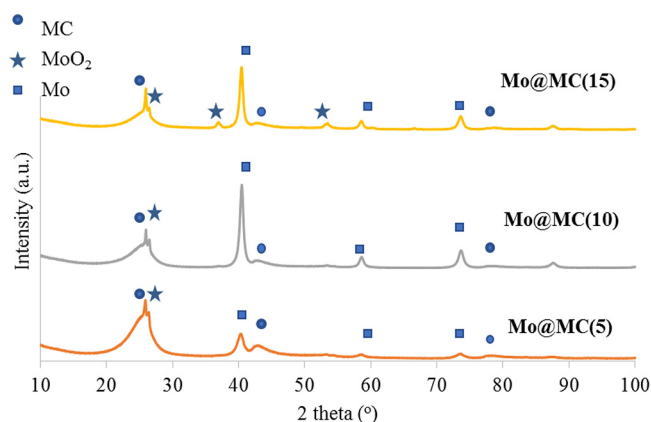
Fig. 4. XRD results of molybdenum incorporated mesoporous carbon catalysts at different metal loadings in their reduced form.

the ability of a material to be heated in the microwave field, corresponding to the mesoporous carbon has not been determined, however, different experimental studies have been found in the literature that provide data for carbon materials, as reviewed by Menendez and coworkers [9]. Based on the data reported by Xing and Yan [46] who determined the dielectric loss tangent for the graphite like mesoporous carbon material as being in the range of 1.0–1.5 depending on the frequency applied during the measurement, the mesoporous material used in this work is supposed to have an excellent microwave absorber ability. As seen in Fig. 3 after the calcination of molybdenum incorporated mesoporous silicate catalysts, MoO_2 crystals are formed. Diffraction peaks observed at 2θ values of 25.99, 36.90, 53.87, 60.87, 67.25° are all corresponding to MoO_2 crystals according to JPDC-01-074-4517. Using Sherrer equation the size of crystals were calculated as 9.8 nm, 27.8 nm and 29.9 nm for Mo@MC(5), Mo@MC(10) and Mo@MC(15), respectively.

Metallic molybdenum crystal was recognized in the structure of all the synthesized catalysts after their reduction (Figs. 4 and 5). Diffraction peaks present at 2θ values of 40.62, 59.60 ve 73.97° are all belonging to metallic molybdenum according to JPDC-00-042-1120. Size of crystals, which was determined using Sherrer equation, is 7.7 nm for Mo@MC(5), 13.5 nm for Mo@MC(10) and 14.3 nm for Mo@MC(15). The particle size obtained from XRD analysis was consistent with the data retrieved from the HRTEM images which was presented in Fig. 5 with the EDX spectrum of the corresponding particles. The molybdenum oxide recognized in the Mo@MC(15) structure could be due to higher metal loading, insufficient reduction or unexpected oxidation of catalysts before the analysis. Since the size of the molybdenum crystals present in the structures of Mo@MC(10) and Mo@MC(15) catalysts were very close to each other, it could be considered that increasing metal loading would not cause any agglomeration. As supported by the HRTEM images presented in Fig. 5, mesoporous carbon is still observed without any significant deformation after reduction. Nitrogen adsorption/desorption isotherms of the calcined molybdenum incorporated mesoporous carbon catalysts having different metal loadings are presented in Fig. 6. Mesoporous carbon in its pure form has Type IV isotherm with type H2 hysteresis loop, according to IUPAC classification. As it is known, this type of hysteresis loop was explained with the Network Model that could be due to interconnected porous network [48]. Surface area of mesoporous carbon was 217 m^2/g and increasing metal loading resulted in a decrease in the surface area of the synthesized catalysts (Table 1). It could be occurred due to some pore blockages. Type IV adsorption desorption isotherms were also seen in the synthesized catalysts attributed that metal incorporation did not collapse the

mesoporous structure, supported by the HRTEM images as well. The pore size distributions of the synthesized catalysts also indicated higher pore blockage observed in the structure of Mo@MC(15) in comparison to the other ones (Fig. 7).

3.2. Catalytic activity results

Molybdenum incorporated mesoporous carbon catalysts were developed with the aim of being used in microwave heated reactor system, and they were firstly tested in conventionally heated system to make enable a comparison (Fig. 8a). The synthesized catalysts show very small activities at temperatures lower than 550 °C. Ammonia decomposition reaction is an endothermic reaction and there is no concern with thermodynamic limitation under these reaction conditions, therefore further increase in temperature enhances the reaction. The maximum ammonia conversion could be obtained in the conventionally heated system was 49%. When the same catalysts were used in microwave heated system, completely different conversion profiles were obtained (Fig. 8b). As indicated in the experimental part, GHSV of ammonia was kept as 36,000 ml/hg$_{cat}$ for both cases. In the microwave heated system, experiments were carried out in a temperature interval starting from 250 °C to 600 °C and conversion of ammonia to hydrogen was achieved even at 300 °C. In Fig. 8a there is no data reported at temperatures lower than 400 °C, since there was no conversion below this temperature. On the contrary, in microwave heated system total conversion was achieved even at 400 °C. While the activity of Mo@MC(15) was negligible in conventionally heated system at 400 °C, it gave total conversion at the same temperature in microwave heated system. The stability test which was performed using this catalyst at 450 °C for 600 min revealed that ammonia conversion value was stable during the reaction period (Fig. 9).

Variations in conversion values obtained using the same catalysts in different systems, namely conventionally heated and microwave heated systems, were generally explained with the differences in the heating mechanisms of these two systems. In conventional heating, heat is transferred from the electrical resistance to the walls and the cavity of the furnace then through the sample by means of sequential conduction and convection mechanisms. As a result, a decrease in temperature can be expected in radial direction for such an endothermic reaction, as seen in the work of Durka et al. [49] whose results showed that temperature near the wall was higher than temperature at the core due to these heat transfer mechanisms. On the other hand, microwave energy is transferred to the catalyst and heat is generated where it is needed. Therefore, the hottest area is supposed to be occurred in the middle of the catalytic bed [49,50]. This situation is known as volumetric heating and it results in formation of inverse temperature profile which is supported by the experimental work of Durka et al. [49]. Higher core temperature comparing to the near wall temperature (inverse temperature profile) as well as prevention of heat loss through the walls and cavity, would be possible reasons of getting better activity in the microwave heated systems [11,8].

The higher conversion that was achieved over molybdenum incorporated mesoporous carbon catalysts under microwave heating could also be explained with the hot spots which are formed due to the difference observed in the microwave absorption ability of metal/-oxides crystals and the support materials [49]. They are also considered as "microplasmas" and their higher local (microscale) temperatures comparing to the average bulk temperature are supposed to increase the conversion [14,16,49]. The enhanced effect of N_2, which is the other product of ammonia decomposition reaction, on the formation of more energetic microplasmas, i.e. hot spots of higher temperature, was also discussed in the literature [16]. Eventhough they could be seen as the electric arcs during the experiments, their temperatures could not be measured by infrared
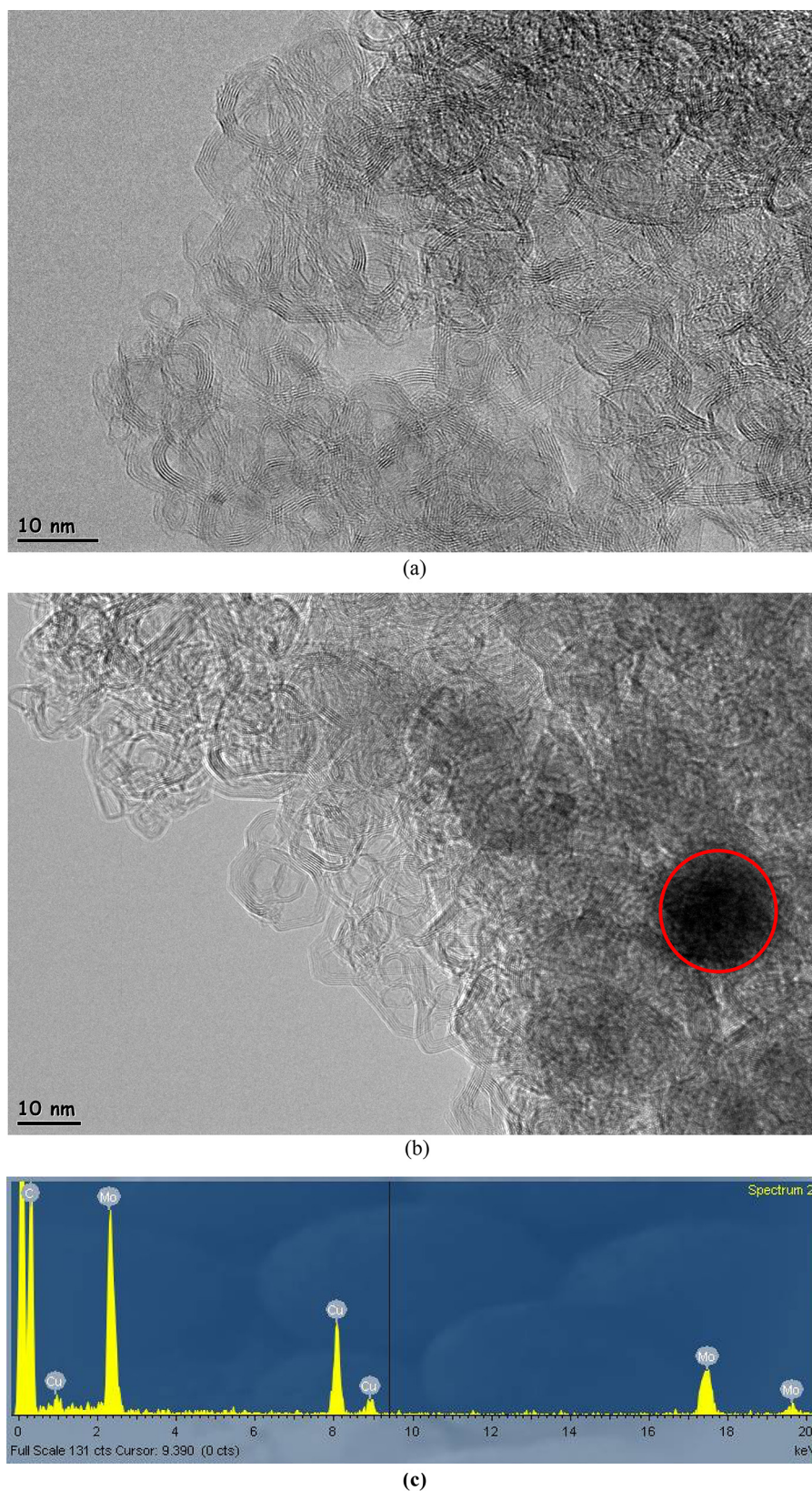
Fig. 5. HRTEM images of (a)mesoporous carbon, (b) reduced Mo@MC(15) (c) EDX analysis of the region given in red circle in part (b). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

pyrometer during the experiments. Durka et al. [51] indicated that infrared pyrometers measured the surface temperature and surface temperature could be close to the bulk temperature if very thin samples were used. Also, measurements of microscopic scale hot spots could not be carried out since infrared pyrometers measured the macroscale temperatures.

Table 1
Physical Properties of Synthesized Catalysts.

Catalyst	wt% Mo (ICP-OES)	Multipoint BET Surface Area (m^2/g)	BJH Adsorption Surface Area (m^2/g)	BJH Adsorption Pore Volume (cc/g)	BJH Adsorption Pore Diameter (nm)
MC	–	216.6	227.8	0.48	2.48
Mo@MC(5)	4.0	211.0	217.8	0.45	2.76
Mo@MC(10)	9.2	199.7	203.5	0.41	2.75
Mo@MC(15)	12.2	187.1	175.3	0.34	2.76
Mo@MC(15)M	*	184.6	197.4	0.61	2.77
Mo@MC(15)C	*	186.1	201.6	0.43	2.76

* ICP-OES analysis was applied to Mo@MC(15) sample before it was used in reaction.

Table 2
Catalytic Activities of Different Catalysts for Ammonia Decomposition Reaction.

Catalyst	Metal Content (wt%)	T(°C)	GHSV(ml/g_{cat} h)	NH_3 conversion (%)	Ref.
Co_7Mo_3/MCM-41	5	600	36,000	99.2	[29]
Mo_{10}/YSZ	10	700	46,000	complete	[27]
MoO_3-G		650	15,000	complete	[42]
MoNx/α-Al_2O_3		650	3600	97.3	[40]
CoMo-I/γ-Al_2O_3	5	600	36,000	99.5	[44]
MoN	bulk	600	6000	97.2	[45]
Ru@graphite carbon	5	550	30,000	95	[32]
Fe@MC(10)C*	7.7	600	36,000	complete	[23]
Fe@MC(10)M**	7.7	450	36,000	complete	[23]
Mo@MC(15)C*	12.2	600	36,000	49	present
Mo@MC(15)M**	12.2	400	36,000	complete	present
Mo@MC(10)M**	9.2	500	36,000	complete	present

* tested in conventional system.
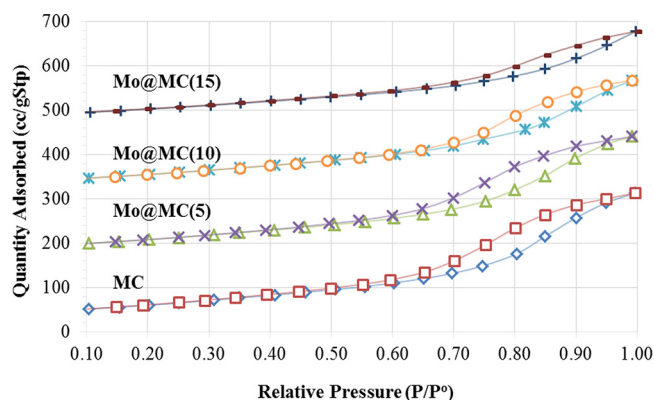** tested in microwave system.

Fig. 6. Nitrogen adsorption/desorption isotherms of molybdenum incorporated mesoporous carbon catalysts in their calcined form.
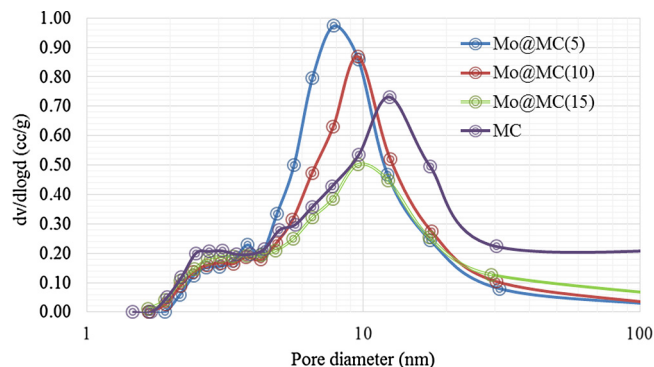

Fig. 7. Pore size distributions of molybdenum incorporated mesoporous carbon catalysts in their calcined form.

In the literature, studies related with the application of molybdenum incorporated catalysts to ammonia decomposition reaction were all carried out in conventionally heated systems. It is known that binding energy of N on transition metal surfaces enhances the utilization of these kinds of metals in ammonia decomposition reaction and the addition of the second metal for tuning the electronic properties and N binding energy, has been considered to enhance the activity. For this reason, to get higher conversion values, bimetallic catalysts that contain Mo and the second transition metal are commonly studied in ammonia decomposition reaction [40,44,45]. Ji et al., [44] showed that Co-Mo bimetallic catalysts gave higher activity than the monometallic Co and Mo catalysts under the same reaction condition (GHSV of 36,000 mLg_{cat}^{-1} h^{-1} at 350–600 °C). The nitrided MoNx/α-Al_2O_3 and NiMoNx/α-Al_2O_3 were also investigated and about 99% conversion was reported at 650 °C with an ammonia feed having GHSV of 1800 h^{-1} by Liang et al. [40]. In this work, they indicated the necessity of nitride or partially nitrided form of the supported NiMo catalysts to obtain high conversion in ammonia decomposition reaction. Podila et al. [45], discussed the importance of the optimum amount for the second metal since higher loading of the second metal could cause a decrease in the activity of the catalyst in ammonia decomposition reaction. They also reported total ammonia conversion at 600 °C with a GHSV of 6000 h^{-1} when bulk molybdenum nitride catalysts were used after nitridation process [45]. As summarized in Table 2, the activity of molybdenum incorporated mesoporous carbon catalysts without any promoter or second transition metal, was comparable or lower than the activity of the catalysts reported in the literature when they were tested in conventionally heated reaction system. On the other hand, application of microwave resulted in a higher activity values at lower reaction temperatures. Total conversion value was achieved over Mo@MC(15) at 400 °C with a $GHSV_{NH3}$ of 36,000 ml/g_{cat} h while 95% ammonia conversion was achieved over Ru@graphite carbon at 550 °C with a $GHSV_{NH3}$ of 30,000 ml/g_{cat} h.

In our previous work, we showed the enhancement in the activities of iron incorporated mesoporous carbon catalyst with the help of microwave heated system. As seen Table 2, a complete conversion could be obtained at 600 °C in conventionally heated system on the contrary the same conversion is achieved at 450 °C
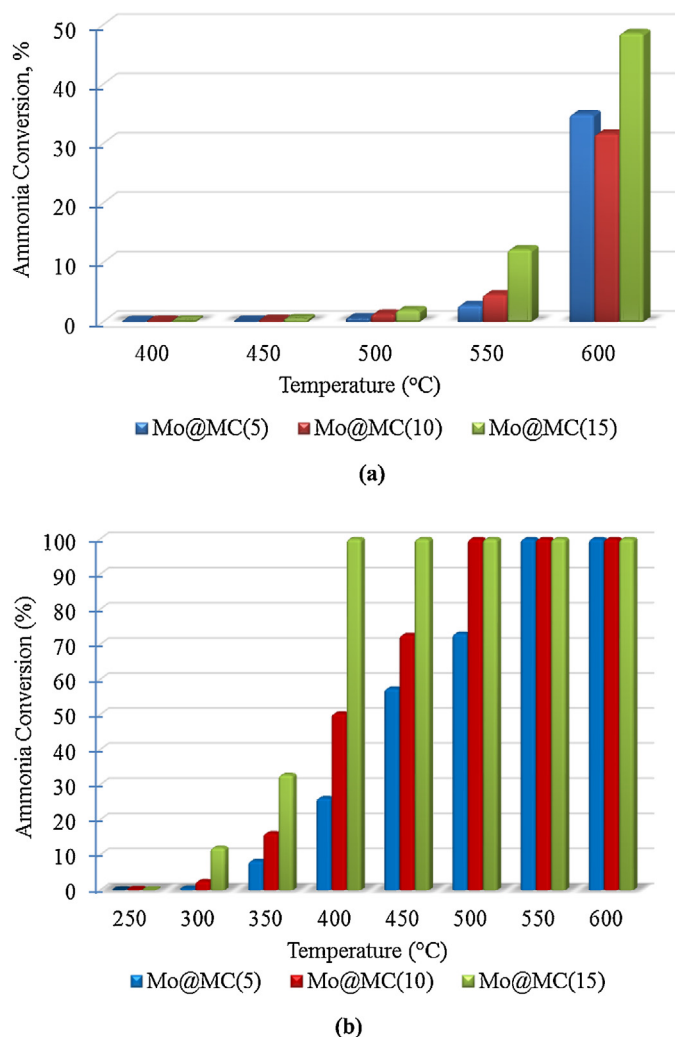
Fig. 8. Variation in conversion with reaction temperature using (a) conventional system (b) microwave system experiments (GHSV$_{NH3}$: 36,000 ml/hg$_{cat}$).
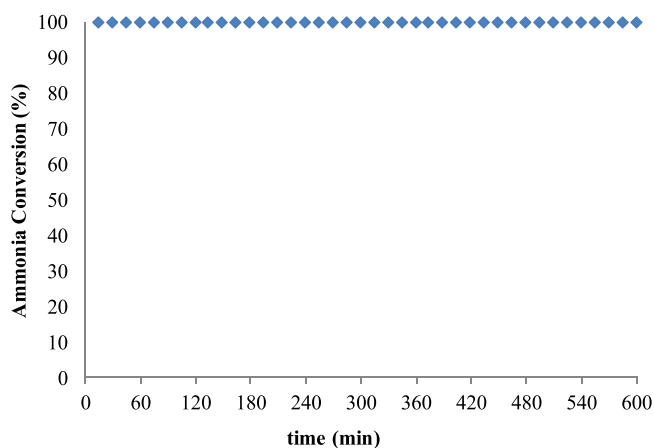

Fig. 9. Decomposition of ammonia as a function of time over molybdenum incorporated mesoporous catalyst (Mo@MC(15)) in microwave heated system at 450 °C with GHSV$_{NH3}$: 36,000 ml/hg$_{cat}$.

in microwave heated system. As followed from the same table, the effect of using microwave heated system is much more considerable in the present study. Eventhough 49% ammonia conversion could be obtained in conventionally heated system, with the utilization of microwave 2 fold higher conversion was achieved at

400 °C. Indeed, this reaction temperature was lower than the values reported in the literature and was adjusted by consuming less than 50 W microwave power. It is expected that the lower operating temperature under microwaves for a given conversion results in a gain in energy efficiency as well.

3.3. Characterization of the catalysts after microwave application

After being tested in ammonia decomposition reaction, molybdenum incorporated catalysts were investigated by XRD technique and the results were presented in Fig. 10. The structure of the mesoporous carbon was still observed without any deformation, as supported by the HRTEM images given in Fig. 13, while metallic molybdenum which had been present before the reaction disappeared in the structure of the spent catalysts resulting in the formation of new phases. As seen in Fig. 10. Mo$_5$N$_6$ is the main phase of molybdenum incorporated catalysts when the reaction was carried out in conventionally heated system. Hexagonal molybdenum nitrides, δ-MoN, is known to crystallize at least three different forms. Ganin et al. [52] described them as δ1-MoN with WC-type structure, formed with stacking faults due to nitrogen atom disorder; δ2-MoN with NiAs-type structure, formed due to ordered array of nitrogen atoms; δ3-MoN formed with a distorted of δ2-MoN structure. Mo$_5$N$_6$, which is seen in this study, is formed due to an intergrowth of the WC- and NiAs-type building blocks, accompanied by vacancies on Mo sites [52]. The formation of molybdenum nitride phases starting from molybdenum oxides during the conventionally heated ammonia decomposition reactions was explained by different groups [40,42,53]. Tagliazucca et al. [42] carried out a detail insitu XRD analysis during ammonia decomposition reaction on MoO$_3$ catalyst which had been prepared by impregnation of molybdic acid solution to activated carbon. They reported that MoO$_3$ paticles converted to molybdenum bronze HxMoO$_3$ and MoO$_2$ at 350 °C and then hexagonal molybdenum nitrides started to be formed between 450 and 500 °C, under the flow of ammonia (15,000 ml/g$_{sample}$ h). For complete nitridation, it is necessary to increase the reaction temperature above 650 °C. Synthesis of δ-MoN phase via the reaction between Mo films with ammonia was also achieved at 998 K for 2 h [54]. Eventhough nitridation was not applied to the synthesized catalysts before the catalytic tests in the present study, X-ray diffraction lines of the spent catalysts showed that reaction conditions favored the formation in molybdenum nitride compounds. Higher activities of molybdenum incorporated catalysts at 600 °C comparing to the activities obtained at lower reaction temperatures, which can be seen in Fig. 8a., may revealed that molybdenum nitride formation from metallic molybdenum species under the flow of ammonia (GHSV 36,000 ml/g$_{cat}$ h) would be much effective at this reaction temperature causing an increase in the activity.

When the catalysts were tested in microwave heated system, it became difficult to recognize the metal nitride phase. Main peaks observed at 2 theta values of 39.3, 52.1 and 61.6° in the structure of the spent catalysts indicated the formation of Mo$_2$C phase. A temperature-programmed reduction-carburization method is known to be one of the most facile conventional method to synthesize high surface area molybdenum carbide from oxide precursor under the flow of hydrogen and methane [36,41]. Considering the short synthesis time and the low synthesis temperature as well as being one step process, microwave application has been also used to synthesize molybdenum carbide [55,56]. Vallance et al. [55] synthesized molybdenum carbide by using carbon with molybdenum metal or trioxide in 90 sn using microwave oven with 800 W power. Yacob et al. [56] applied microwave irradiation (with a power usage of 800 W) to the mixture of ammonium heptamolybdate solution and carbon black powder and they obtained molybdenum carbide after 2 min. They mentioned that carbon acted as a reduc-
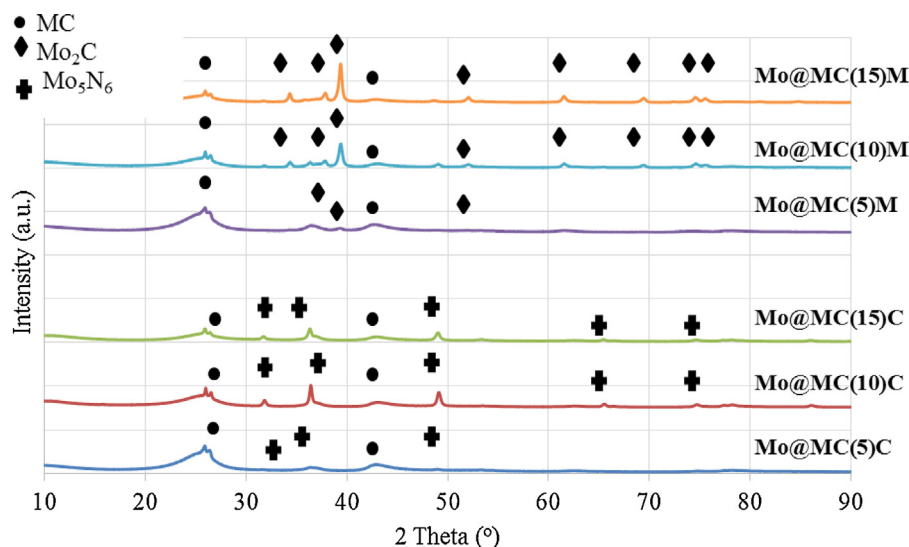
Fig. 10. XRD results of the molybdenum incorporated mesoporous carbon catalysts in their used form.

ing agent and it reduced molybdenum oxide to molybdenum so that Mo_2C was formed. In our study, molybdenum incorporated mesoporous carbon catalysts were reduced before the reaction and carbide crystals were formed between metallic molybdenum and carbon support with the help of the microwave irradiation having a power of less than 50 W. It is supposed to be occurred within a few minutes [55,56]. In the experimental and theoretical study on molybdenum carbide and nitride species for ammonia decomposition reaction, carried out by Zheng et al. [41] it was mentioned that fresh Mo_2C catalyst started to show smaller carbide and nitride crystals after 4 h of conventionally heated ammonia decomposition reaction at 600 °C and only molybdenum nitride phase after 100 h. According to their theoretical calculations, adsorbed N atoms tend to form surface or subsurface nitride and further bulk nitride after the cleavage of N—H bond and nitridation of Mo_2C is supposed to be occurred from the surface to the bulk. Eventhough XRD analysis of our samples were carried out after being used in the microwave heated reaction system up to a reaction temperature of 600 °C, it is really hard to see the molybdenum nitride species as followed from Fig. 10. It is known that metal nitride species are air sensitive, so there is a possibility of oxidation of molybdenum nitride crystallites resulted in the formation of molybdenum oxide [45]. However, neither nitride nor oxide species are determined from X-ray diffraction analysis of the samples being used in microwave heated system. Moreover, Zheng et al. reported that ammonia conversion value decreased from 85% to 71% in first 20 h of reaction experiments at 600 °C due to changes in the catalyst structure [41]. Since the total conversion of ammonia was achieved at much lower reaction temperature, 400 °C, changes in the structure of the catalysts are not expected and as presented in Fig. 9, the activity of molybdenum incorporated mesoporous catalyst was highly stable within 10 h of reaction. Therefore, it can be said that molybdenum carbide crystals are formed and stayed with high stability throughout the reaction. In the work of Zheng et al. [41] the apparent activation energy for ammonia decomposition over Mo_2C was calculated by using Arrhenius equation in the temperature region of 450–600 °C and it was reported as about 89 kJ/mol. Their estimation for 2 wt% Ru incorporated carbon supported catalysts was 75–85 kJ/mol indicating that Mo_2C has a great potential for replacing Ru in ammonia decomposition reaction [57]. Considering the difference in the activity of the catalysts on ammonia decomposition reaction in microwave system in comparison to the conventionally heated system (Fig. 8), it can be said that formation of Mo_2C due to microwave appli-
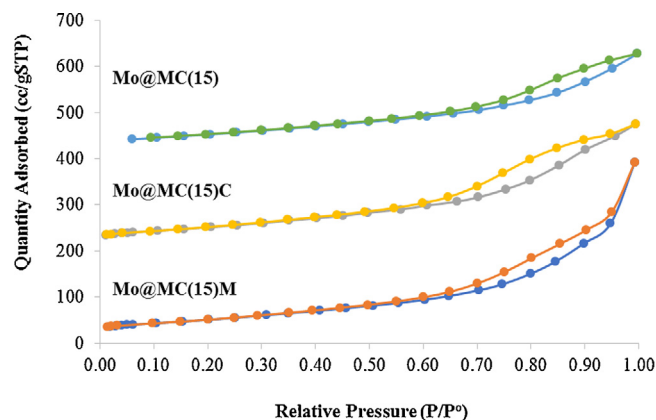

Fig. 11. Nitrogen adsorption/desorption isotherms the molybdenum incorporated mesoporous carbon catalysts in their used form.

cation has a great contribution to the higher performance of this type of catalysts in ammonia decomposition reaction, besides the enhancing effects of microwave application discussed in Section 3.2.

In the literature, microwave-specific effect has been also discussed, especially for gas-carbon reactions. It was reported that specific microwave effects on the mechanism was proposed as the reason of a great change in the apparent thermodynamic of the reaction resulting in higher conversion values at lower reaction temperatures [58,59]. Since the application of microwave radiation in ammonia decomposition reaction is a new subject, it is expected that further studies using transition metal incorporated carbon catalysts may provide new insights to clarify the specific microwave effects on this reaction.

The nitrogen adsorption/desorption isotherms of Mo@MC(15) catalysts in its used forms, namely Mo@MC(15)M and Mo@MC(15)C, were plotted in Fig. 11. After being used in either the conventional system or microwave system, BET total surface area of Mo@MC(15) catalyst did not change, as seen in Table 1. However, an increase in pore volume was clearly seen. Eventhough the average pore dimeter values were same for fresh and spent forms of catalysts, a different pore size distribution was observed in pore size distribution (Fig. 12). However, these differences were not so high indicating that microwave application
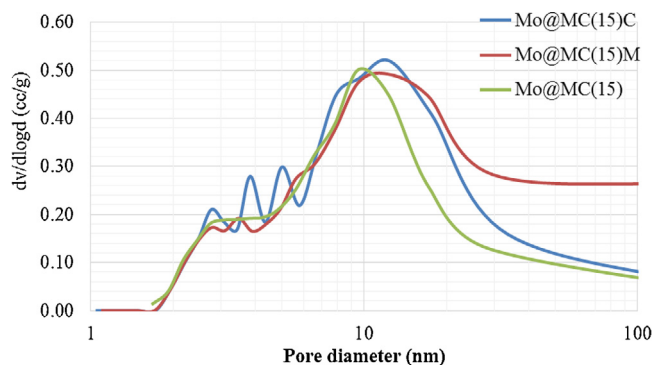
Fig. 12. Pore size distribution of the molybdenum incorporated mesoporous carbon catalysts in their used form.
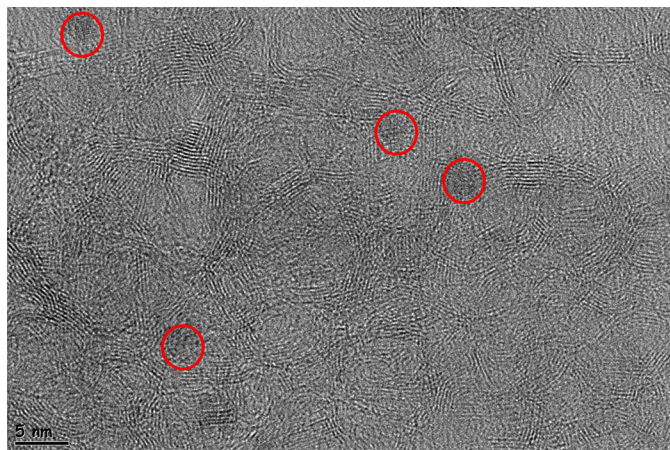

Fig. 13. HRTEM images of Mo@MC(15) after being tested in microwave heated system.

had no significant effect on the catalyst pore structure as supported by the HRTEM analysis given in Fig. 13.

4. Conclusions

Molybdenum incorporated mesoporous carbon catalysts were prepared following the impregnation procedure and they were used in microwave-assisted ammonia decomposition reaction. When the activities of the synthesized catalysts were evaluated in the conventional System with a GHSV of 36,000 ml/hg$_{cat}$, lower activity values were observed below 550 °C and the highest ammonia conversion was about 50%. In the case of microwave system, conversion of ammonia was observed at temperatures as low as 300 °C and a complete conversion was achieved at 400 °C, over the catalyst, which contained 12 wt% Mo, at (with GHSV of 36,000 ml/hg$_{cat}$). In microwave heated system, microwave energy is transferred directly to the active particles instead of heat transfer and this contributes to the higher activity of the catalysts. Formation of hot spots, which were also considered as "microplasmas", within the catalytic bed was considered as another possible reason of an increase in the catalyst activity, as compared to conventionally heated system. Microwave application to the metallic molybdenum particles caused formation of molybdenum carbide and the reaction studies showed that these carbides were highly active in ammonia decomposition reaction.

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